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# PATENT SPECIFICATION

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## (54) AQUEOUS DISPERSIONS OF COPOLYMERS OF MONOESTERS OF OLEFINICALLY UNSATURATED DICARBOXYLIC ACIDS

(71) We, BADISCHE ANILIN- & SODA-FABRIK AKTIEN-GESELLSCHAFT, a German Joint Stock Company of 6700 Ludwigshafen, Federal Republic of Germany, do hereby declare the invention, for which we pray that a Patent may be granted to us, and the method by which it is to be performed to be particularly described in and by the following statement:—

This invention relates to new polymer dispersions. In the production of copolymer emulsions small amounts of water-soluble monomers are often added to improve the mechanical stability or the resistance to electrolytes and other auxiliaries. Examples of water-soluble monomers are acrylic acid, methacrylic acid and vinylsulfonic acid. The addition of these acids in many cases offers a number of advantages, such as improved adhesion of film prepared from the dispersions, or improved hydrophilic properties of the polymer. The acid groups are also amenable to crosslinking reactions.

It is known from German Laid-open Specification 1,221,748 that butadiene/styrene copolymers can be prepared which contain up to 10 percent of polymerised units of a monoolefinically unsaturated acid such as acrylic acid, itaconic acid, vinylsulfonic acid, vinylbenzoic acid and isopropylbenzoic acid. German Laid-open Specification 1,470,774 describes copolymers containing units of an unsaturated monobasic organic acid and, additionally, units of a dibasic unsaturated organic acid. Examples of unsaturated monobasic acids are acrylic acid, methacrylic acid and crotonic acid, and examples of dibasic acids are maleic acid, fumaric acid and itaconic acid. Emulsion polymerization of vinylsulfonic acid is described for example in Houben-Weyl "Methoden der organischen Chemie", volume 14/1, 4th edition, pages 189 et seq. The copolymerization of other sulfonic acids having an ethylenically unsaturated group, for example orthostyrenesulfonic, metastyrenesulfonic or parastyrenesulfonic acid and similar acids bearing substituents on the benzene nucleus and of acids in which the sulfonic acid group is attached to a heterocyclic ring, for example 2-sulfo-5-allylfuran, 2-sulfo-4-vinylfuran and 2-sulfo-5-vinylthiophene with N,N'-methylene-bisacrylamide for the synthesis of ion exchangers is disclosed in U.S. Patent 1,527,300.

The use of the said acids is however accompanied by a number of disadvantages. Thus it is known that dispersions of copolymers containing a fairly large aount of polymerized units of acrylic acid thicken in an alkaline medium and this is undesirable in many cases. Vinylsulfonic acid will not polymerize with a number of monomers such as butadiene, isobutylene and allyl alcohol (cf. J.Polym.Sci., 27, 295, 1958).

We have now found that aqueous dispersions of copolymers of olefinically unsaturated monomers which contain 0.1 to

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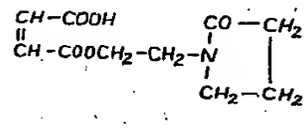
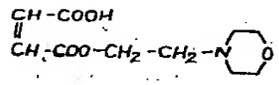
20% by weight of the total weight of the polymer of polymerized units of a monoester of maleic or fumaric acid or a salt thereof are particularly stable when the ester group of the monoester has the general formula (I):—

$$—COO—CH_2—CH_2—R \quad (I)$$

in which R is N-pyrrolidonyl, N-morpholinyl or O-alkyl of one to four carbon atoms. The $—OCH_3$ radical is of particular interest as the O-alkyl radical. The following are examples of such monoesters:





CH—COOH
‖
CH—$COOCH_2—CH_2—OCH_3$

Monomers having ester groups of the general formula (I) may be obtained by a conventional method by reaction of maleic anhydride or by transesterification of a monoester of maleic or fumaric acid such as the methyl, ethyl or n-butyl ester, with an alcohol of the general formula (II)

$$HOCH_2—CH_2—R \quad (II)$$

in which R has the meaning given above for formula (I) under otherwise conventional conditions. The acid chlorides of maleic and fumaric acid may also be used instead of maleic anhydride or a maleic or fumaric monoester.

The copolymer dispersions may readily be prepared by known methods, have good mechanical stability and usually froth less than prior art copolymer dispersions. For use as binders for coating compositions for paper smaller amounts of copolymerizable acids are necessary to achieve a given rolling stability than when using for example conventional carboxylic or sulfonic acids.

Examples of comonomers which may be polymerized with the monoesters are monovinylaromatic monomers which like styrene, $\alpha$-methylstyrene, o-chlorostyrene and vinyltoluene have a benzene nucleus and eight to nine carbon atoms, $\alpha,\beta$-olefinically unsaturated carboxylic nitriles such as acrylonitrile and methacrylonitrile, the alkyl esters, anhydrides and salts of unsaturated polymerizable monocarboxylic and dicarboxylic acids, for example of acrylic acid and its $\alpha$-substituted and $\beta$-substituted derivatives such as methacrylic acid, crotonic acid, maleic acid, fumaric acid and itaconic acid, 1,3-dienes such as particularly butadiene, vinyl esters such as vinyl acetate, vinyl propionate, vinyl n-butyrate, vinyl laurate and vinyl stearate, vinyl halides such as vinyl chloride and vinylidene chloride, and also vinyl ethers, vinylcarbazole, vinylpyridine and vinyl lactams such as vinylpyrrolidone and vinylcaprolactam. Comonomers of great interest are monoolefinically unsaturated carboxylic esters of four to twenty-two carbon atoms, for example vinyl esters of saturated linear or branched monocarboxylic acids and/or esters of $\alpha,\beta$-olefinically unsaturated $C_3$ to $C_5$ monocarboxylic or dicarboxylic acids and $C_1$ to $C_{18}$, particularly $C_2$ to $C_8$, linear or branched alkanols such as the esters of acrylic and methacrylic acids with methyl, ethyl, isopropyl, n-butyl, isobutyl, tert.-butyl, n-hexyl, 2-ethylhexyl and lauryl alcohol and also dimethyl maleate, diethyl maleate and di-n-butyl maleate. The nitriles, particularly acrylonitrile, are often used in amounts of up to 50% by weight, particularly in amounts of from 0 to 40% by weight, preferably in amounts of from 4 to 29% by weight based on the whole of the monomers (or the weight of the polymer).

In addition to these monomers, small amounts, generally from 0 to 15% by weight based on the whole of the monomers (i.e. the weight of polymer) of other monomer units may be introduced which bear groups which after the polymerization are accessible for another condensation or addition reaction and thus permit modification of the films prepared from the dispersions. Examples of these are olefinically unsaturated monomers which have an acid amide, acid imide, N-methylolamide or N-methylol etheramide group such as acrylamide, methacrylamide, N-methylolacrylamide and N-methylolmethacrylamide, acryloylurea and methacryloylurea, N-acryloylcyandiamide, N-n-butoxymethylacrylamide and N-n-butoxymethacrylamide and also the methyl, ethyl, and propyl ethers of N-methylolmethacrylamide and N-methylolacrylamide. Among these special significance attaches to the amides and N-methoxymethylamides and also the N-hydroxymethylamides of $\alpha,\beta$-monoolefinically unsaturated $C_3$ to $C_4$ monocarboxylic acids. Other hydrophilic monomers such as $\alpha,\beta$-monoolefinically unsaturated $C_3$ to $C_5$ monocarboxylic and dicarboxylic acids, for example acrylic acid, methacrylic acid and

itaconic acid, or ethylene glycol or butanediol monoacrylate or monomethacrylate and also N-hydroxyethylpyrrolidone acrylate units may also be introduced into the polymers in small amounts, generally of up to 15% by weight, particularly from up to 10% by weight based on the whole of the monomers. Unsaturated carboxylic acids are of special interest.

The copolymers generally contain from 70 to 99.9% of their weight of units of monomers of the type specified above which when polymerized alone give homopolymers which are insoluble in water, such as styrene, butadiene, acrylonitrile, acrylic esters, methacrylic esters, vinyl halides and vinyl esters. The proportion of such monomers is preferably from 70 to 95%. The concentration of the dispersion in the copolymers may be varied within wide limits. It is generally from 40 to 65% by weight of copolymer based on the whole dispersion.

Copolymer dispersions according to the invention may be used in the conventional fields of application of polymer dispersions. Copolymers having a content of from 0.5 to 3% of their weight of polymerized units of monoesters are preferred for use as binders for coating compositions for paper and nonwoven textile fabrics, for coating leather, for the production of waterproof textile finishes, for the production of needle felt floor coverings and finally for the production of coatings on concrete or wood. Copolymer dispersions having a content of from 3 to 10% of their weight of maleic monoesters and/or fumaric monoesters are preferred for use for priming leather and also in the water-repellent finishing of textile fabrics and as a dispersing agent for pigments.

The aqueous copolymer dispersions may be prepared by a conventional method by polymerization of the monomers in aqueous emulsion under the conventional conditions of pressure and temperature.

In the polymerization in aqueous emulsion the conventional dispersing and emulsifying agents are generally used in somewhat smaller amounts than otherwise usual. Conventional water-soluble per compounds such as hydrogen peroxide, potassium persulfate, sodium persulfate, cumene hydroperoxide and lauroyl peroxide, and also azobisisobutyronitrile and conventional redox initiators may be used as polymerization catalysts. The polymerization temperature is generally from 5° to 100°C. Activating radiation of a wavelength $\lambda$ more than 450 m$\mu$ may also be used in some cases to accelerate the polymerization. The monoesters may be present wholly or partly in the form of their salts, for example their ammonium, sodium or potassium salts in the polymerization. The salts are usually present in the aqueous medium in dissociated form. In the polymers, the polymerized monoester units are also often present in dissociated form, i.e. the polymers sometimes have free carboxyl groups stemming from the monoester units and carboxylate anions ($-COO^{(-)}$ groups) and undissociated salt groups (for example $-COONH_4$ groups) may be present at the same time.

The Examples illustrate the invention. Parts and percentages are by weight unless otherwise stated. K values have been determined according to H. Fikentscher, Cellulose Chemie, volume 13, 58 (1932).

## EXAMPLE 1.

10 parts of a mixture of 289 parts of water, 15 parts of methacrylamide, 15 parts of acrylamide, 460 parts of methyl acrylate, 5 parts of the sodium salt of the maleic monoester of N-$\beta$-hydroxyethylpyrrolidone (prepared by reaction of equimolar amounts of maleic anhydride and N-$\beta$-hydroxyethylpyrrolidone at from 58° to 70°C followed by neutralization of the reaction product with sodium hydrogen carbonate), 24.7 parts of a 35% aqueous solution of the sulfated reaction product of 50 moles of ethylene oxide with 1 mole of p-iso-octylphenol and 3 parts of a 50% aqueous solution of turkey red oil is added at 20°C to a mixutre of 100 parts of water and 0.1 part of ascorbic acid. The whole is heated to 30°C and at the same time the remainder of the monomer mixture and a solution of 1 part of sodium persulfate in 40 parts of water and a solution of 1.5 parts of sodium bisulfite in 35 parts of water are added over two hours. Polymerization is continued for another hour at 50°C and an aqueous dispersion is obtained having a solids content of 46.7% by weight. The copolymer has the K value 98 and the dispersion has the LD value 80%. The dispersion is suitable particularly as a binder for the production of nonwoven fabrics.

## EXAMPLE 2.

0.5 part of a commercial $C_{16}$ alkyl sulfate in 200 parts of water is heated to 80°C and there is added thereto a mixture of 250 parts of n-butyl acrylate, 250 parts of styrene, 20 parts of acrylamide, 5 parts of tetrasodium pyrophosphate, 5 parts of the acrylic ester of N-$\beta$-hydroxyethylpyrrolidone and 10 parts of the sodium salt of the mono-$\beta$-methoxyethyl ester of maleic acid, prepared like the monoester used in Example 1 but with monomethoxyethylene glycol as the alcohol component. The pH of the mixture is adjusted to 5.6 and then a mixture of 10 parts of ammonium persulfate in 50 parts of

water is added over two hours. After the persulfate has been added polymerization is continued at 90°C for one hour and a copolymer dispersion is obtained having a solids content of 49% by weight. The copolymer has a K value of 48. The LD value of the dispersion is 60%. The dispersion is suitable particularly for the production of coating compositions for paper which have a stable pH and are low lather.

EXAMPLE 3.

100 parts of water, 1.2 parts of sodium lauryl sulfate and 2 parts of potassium persulfate are heated to 100°C and there is then metered in over four hours at 100°C as a feed a mixture of 315 parts of water, 8.5 parts of sodium lauryl sulfate, 1.5 parts of sodium pyrophosphate, 290 parts of styrene, 8.0 parts of acrylic acid, 2 parts of acrylamide, 6 parts of the potassium salt of β-N-morpholinylethyl monomaleate, 195 parts of butadiene and 40 parts of a 25% solution of potassium persulfate. 5.7 parts of 25% ammonia solution is added after cooling. A dispersion is obtained which has an LD value of 63, a pH of 7.8 and a solid content of 50.1% by weight.

The dispersion is suitable for surface finishing paper, textiles, wood and concrete.

EXAMPLE 4.

The procedure described in Example 3 is adopted but vinyl acetate is used instead of styrene and ethyl acrylate is used instead of butadiene. A copolymer dispersion is obtained having a pH of 7.5, an LD value of 84 and a solids content of 50.6%. The dispersion is suitable as a coating agent for wood and concrete.

WHAT WE CLAIM IS:—

1. An aqueous dispersion of a copolymer of olefinically unsaturated monomers which contains from 0.1 to 20% by weight of the total weight of the polymer of polymerized units of a monoester of maleic or fumaric acid or a salt thereof, wherein the ester group of the monoester has the general formula (I):—

$$—COO—CH_2—CH_2—R \qquad (I)$$

in which R is N-pyrrolidonyl, N-morpholinyl or $C_1$ to $C_4$ O-alkyl.

2. An aqueous dispersion as claimed in claim 1 wherein the O-alkyl is $—OCH_3$.

3. An aqueous dispersion as claimed in claim 1 or 2, wherein the copolymer also contains polymerized units of one or more monomers selected from monoolefinically unsaturated carboxylic esters of 4 to 22 carbon atoms, 1,3-dienes and monovinyl aromatic monomers of 8 or 9 carbon atoms with or without up to 50% by weight of units of α,β-olefinically unsaturated carboxylic nitrile units and/or up to 15% by weight of monomer units bearing a group accessible for further condensation or addition.

4. An aqueous dispersion as claimed in any of claims 1 to 3 wherein the copolymer contains from 0.5 to 3% by weight of the total weight of the polymer of polymerized units of a monoester as specified in claim 1.

5. An aqueous dispersion as claimed in any of claims 1 to 3 wherein the copolymer contains from 3 to 10% by weight of the total weight of the polymer of polymerized units of a monoester as specified in claim 1.

6. An aqueous dispersion as claimed in claim 1 and specified in any of the foregoing Examples 1 to 4.

J. Y. & G. W. JOHNSON,
Furnival House,
14—18 High Holborn,
London WC1V 6DE.
Chartered Patent Agents,
Agents for the Applicants.

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